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HIGH TEMPERATURE GAS ENERGY TRANSFER.(U)
AUG 78 B S RABINOVITCH

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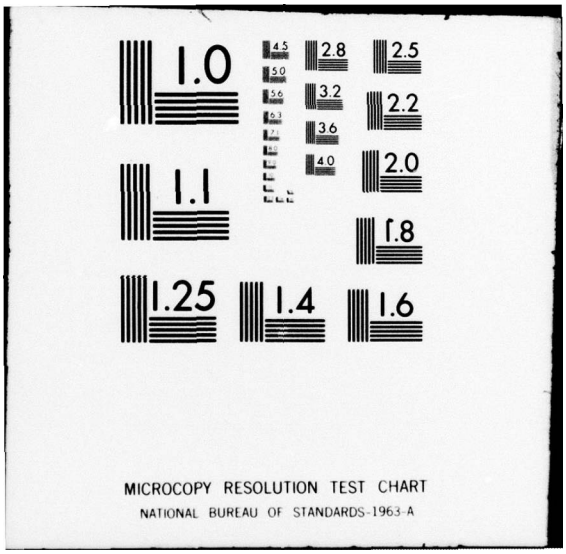
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ANNUAL SUMMARY REPORT, 1 March 1977 - 31 July 1978

(6) High Temperature Gas Energy Transfer,

(10) B. S. Rabinovitch, Principal Investigator
Department of Chemistry, BG-10
University of Washington
Seattle, Washington 98195

(9) Annual Summary rept. 1 Mar 77-31 Jul 78,

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(15) Contract N00014-75-C-0690

Project NR 092-549

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(11) 15 August 1978 (12) 10p.

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This report bridges a longer period in which the anniversary date of the contract was extended to 31 July.

I. Complete listing of technical reports:

1. Technical Report TR01, 7 January 1976.
Vibrational Energy Transfer in Reaction Systems at Elevated Temperatures by B. S. Rabinovitch, D. G. Keil, J. F. Burkhalter and G. B. Skinner.

In this report a theoretical analysis was given of shock tube data for high temperature gas reactions. The data were analysed to show that collisional energy transfer efficiency appears to decrease at high temperatures.

2. Technical Report TR02, 20 April 1976
Temperature Dependence of the Arrhenius Activation Energy. High Temperature Limit by J. F. Burkhalter and B. S. Rabinovitch.

In this report a conventional approximation to the high temperature vibrational partition function is shown to be defective, and the usual high temperature expression for the Arrhenius activation is in error. The variation of the activation energy for unimolecular reactions as a function of temperature is calculated for various representative systems.

3. Technical Report TR03, 15 October 1976
Intermolecular Vibrational Energy Transfer in Thermal Unimolecular Systems by D. C. Tardy and B. S. Rabinovitch.

This report gives a comprehensive and detailed survey and analysis of energy transfer in thermal gaseous systems. The present status of the field is delineated and future areas of work indicated.

The following were submitted in the period covered by the present report:

4. Technical Report TR04, 15 April 1977
On the Use of Exact Vibrational State Counting Methods in RRKM Rate Calculations by S. E. Stein and B. S. Rabinovitch

This report describes an algorithm for accurate state sum and density calculations and refutes an error in the literature.

5. Technical Report TR05, 15 August 1977
Vibrational Translational Energy Transfer in Atom-Polyatomic Molecule Collisions in Thermal Reaction Systems by I. Oref and B. S. Rabinovitch.

In this report a simple theoretical model describing energy transfer probabilities is given. Conservation of angular momentum was imposed. The importance of completeness and detailed balance conditions and correction of an earlier model in the literature are illustrated. The model is applied to experimental data.

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6. Technical Report TR06, 1 September 1977
Problems of Diffusion in a Low Pressure Gas Stream as Related to the Polanyi Diffusion Flame (Cloud) Method by D. G. Keil, J. F. Burkhalter and B. S. Rabinovitch.

A theoretical and experimental study was made of flow and diffusion of a reactant in a low pressure gas stream. Connection is made with earlier theoretical analysis.

7. Technical Report TR07, in preparation
Do Highly Excited Reactive Polyatomic Molecules Behave Ergodically?
by I. Oref and B. S. Rabinovitch.

The literature is surveyed and analysed. A variety of excitation techniques including crossed molecular beam, laser, chemical activation, photochemical and thermal are considered. The answer to the title question is "yes." The relationship to the present work on intermolecular transfer is the following: multiphoton laser experiments frequently involve collisional heating of the gas. In order to understand the results, one must have a good basis for interpretation of data. In this survey, some suggested models for energy relaxation by molecular collisions are criticized and data reinterpreted in light of results obtained in this laboratory.

II. Listing of publications.

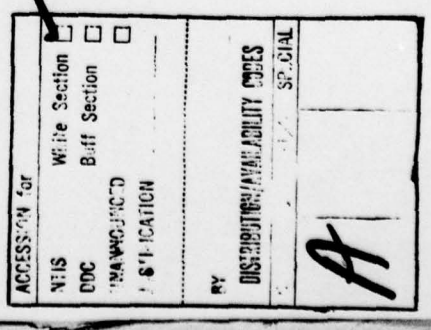
1. Vibrational Energy Transfer in Reaction Systems at Elevated Temperatures, Proceed. Tenth Internat. Shock Tube Sympos. ed. G. Kamimoto, Kyoto, 1976.

2. Intermolecular Vibrational Energy Transfer in Thermal Unimolecular Systems. D. C. Tardy and B. S. Rabinovitch, Chem. Revs., 77, 369 (1977).

3. On the Use of Exact Vibrational State Counting Methods in RRKM Rate Calculations by S. E. Stein and B. S. Rabinovitch, Chem. Phys. Lett., 49, 183 (1977).

4. Vibrational Translational Energy Transfer in Atom-Polyatomic Molecule Collisions in Thermal Reaction Systems, I. Oref and B. S. Rabinovitch, Chem. Phys., 26, 385 (1977).

5. Problems of Diffusion in a Low Pressure Gas Stream as Related to the Polanyi Diffusion Flame (Cloud) Method, D. G. Keil, J. F. Burkhalter and B. S. Rabinovitch, J. Phys. Chem., 82, 355 (1978).



III. Current Work

The following additional accomplishment, not covered in the current Technical Reports, has been made:

A. Theoretical

1. Analysis of flow, diffusion and reaction

The analysis of the diffusion cloud system has been being extended to consideration of laminar flow with wall reflection. In our experiments on the diffusion of mercury (see Technical Report TR06) the diffusant concentration could be calculated using an infinite space flat velocity model as long as $\frac{\mu}{2D}$ is sufficiently large. In thermal cyclopropane experiments, this is no longer possible. The higher diffusion coefficients at high temperatures mean that the reactant moves out from the axis significantly. Reflection at the wall begins to change the concentration profile. For these experiments, a model suggested by Nevrovskii was used[1] which gives a more precise model with a laminar flow field. A general solution was not given by him. Programs are currently being written to calculate these concentrations. The problem resolves itself into the solution of hypergeometric equations. So far we have been able to calculate 10 eigenvalues for the series. It appears the reactant actually experiences a velocity approximately equal to the average velocity $\bar{u}$.

2. Stochastic Calculations.

New computer programs have been written for the process of collisional activation deactivation for single and multiple reaction channel systems — including termination of reaction after any assigned number of collisions as occurs in the gas-surface activation systems. Matrix multiplication for almost any size matrix are handled — order 600 have been the largest necessary so far.

B. Experimental Work

1. Diffusion Cloud Method

Experiments have been completed at 975K and 1175K with inert gases He, H_2, N_2 and CO_2 in the cyclopropane reaction system.

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[1] Nevrovskii, V.A., Kinetike Kataliz, 16, 823-832 (1975).

a) Relative efficiencies and absolute rates were measured in great detail at 975K. The range of pressures in the reactor were 0.53, 1.0 and 2.0 torr. The relative efficiencies ($CO_2 \equiv 1$) are as follows:

p(torr)	CO_2	N_2	H_2	He
0.5	1	0.4	0.17	0.17
1.0	1	0.70	0.35	0.40
2.0	1	0.67	0.50	0.50

Good general agreement exists. Analysis of the data is continuing. The relative efficiency of weaker colliders tends to decrease at lower pressures. This accords with theoretical predictions on the relative efficiency quantity defined by Tardy and Rabinovitch as $\bar{\beta}'(\infty)$. The values of $\bar{\beta}'$ yield tentative results for the average down jump size $\langle \Delta E \rangle_d$ on collisions between the bath gas and hot (reactive) cyclopropane molecules as follows (step ladder model):

Bath Gas	$\langle \Delta E \rangle_d$ (cm^{-1})
He	300
H_2	200
N_2	800
CO_2	1200

These values make good general sense. They illustrate the greatly reduced values of collision efficiency that occur at temperatures of 1000K (and higher) and which invalidate most earlier treatments of high temperature shock tube and laser systems. We exempt our own report TR01 from this criticism!

b) Temperature dependence of collisional energy transfer efficiencies were measured between 975K and 1175K. They are presented in the form of Arrhenius activation energies, E_a. These are not necessarily final values.

p, torr	E_a (kcal $mole^{-1}$)			
	CO_2	N_2	H_2	He
0.53	47	--	--	43
1.0	42	44	--	--
2.1	40	42	45	48
7.2	--	--	42	--

Despite apparent scatter in the data which makes us unhappy and which is still being analysed in terms of more sophisticated hydrodynamic models, the low values of E_a bring out clearly beyond experimental error that a significant decrease in $\langle \Delta E \rangle_d$ (i.e., collisional efficiency) occurs with temperature rise. The Arrhenius E_a values are approximately 7-15 kcal lower than would exist for a strong collider at the region of fall off involved (a factor of 2 decrease in efficiency causes a decrease in Arrhenius E_a of $\sim$ 5 kcal).

2. Gas-Surface Energy Transfer. Variable Encounter Method

Work by our simple beam-less pseudo-molecular beam method has progressed excellently. Two separate groups are working on this technique which we are stressing heavily because I believe that we have made a real advance in the study of energy transfer in the transient region of behavior.

a) Cyclopropane. Measurements have been made over the range of temperatures from 770K to 1150K in reactors of encounter number 1, 2 and 8. The effect of the transient behavior is clearly evident. The work is continuing. Reproducibility is excellent.

b) Cyclopropane-d_2. Measurements have been made over the temperature range 800K to 1170K in reactors of encounter number 2 and 40. Competitive channel as well as total reaction are monitored. Again the effect of transients is clearly demonstrated.

It is now established that the wall is a more efficient collider than the parent gas molecules. The value of $\langle \Delta E \rangle_d$ at 1000K is $\sim$ 3500 cm^{-1}. The corresponding value for the parent molecule is only $\sim$ 1700 cm^{-1}.

We are currently constructing a new apparatus to permit controlled variation of the initial temperature.

IV. Personnel

The following graduate students and fellows have been involved on this project in the period.

Barrie Barton
John Burkhalter
David Kelley
Dr. Efstathios Kamaratos
Dr. Lajos Zalotai (Visiting Assist. Professor from Zeged, Hungary on U.N. Fellowship)

V. Work under this project was reported in lectures at five universities in Israel and at the Laser Conference, Jerusalem, Jan. 1978; at 12 universities in U.K. and at a mini-symposium on Unimolecular Reactions at Leeds University, Feb.-July, 1978; and at the University of Göttingen and Max Planck Institute für Stromungforschung.

B. S. Rabinovitch
Principal Investigator

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Gases	Vibrational Energy
High Temperature	Wall Activation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Work under this contract is summarized. Results on vibrational energy transfer and temperature dependence by the Diffusion Cloud method are described; also, results by a novel and simple Variable Encounter Method for the study of vibrational energy transfer between gas molecules and a wall at high temperatures and levels of activation in the transient region.

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